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(54) Title: CATALYST COMPOSITIONS AND PROCESSES FOR OLEFIN OLIGOMERIZATION AND POLYMERIZATION			
(57) Abstract			
<p>The present invention is directed to certain novel late transition metal pyrrolaldimine chelates and, further, to novel bidentate ligand compounds of substituted pyrrolaldimine, and their utility as polymerization catalysts in processes of polymerizing olefin monomers and copolymerizing olefin monomers with functionalized alpha-olefin monomers.</p>			

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**CATALYST COMPOSITIONS AND PROCESSES
FOR OLEFIN OLIGOMERIZATION AND POLYMERIZATION**

This application is a continuation-in-part
5 application of copending U.S. application Serial No.
08/822,536, filed March 24, 1997.

This invention was made with United States
Government support under Contract No. 70NANB5H1136
awarded by the Department of Commerce's National
10 Institute of Standards and Technology. The United States
has certain rights in the invention.

The present invention is directed to organometallic
catalysts and catalyst compositions useful in the
oligomerization or polymerization of alpha-olefins alone
15 or in combination with functionalized olefins, certain
bidentate ligand compounds useful in providing the
subject catalysts, processes of forming the bidentate
ligand compounds and catalysts therefrom, processes of
forming olefin oligomers and polymers utilizing the
20 subject catalysts, and catalyst compositions and the
oligomers and polymers formed therefrom.

The polyolefin industry has relied on various
catalyst and initiator systems. The polymerization of
ethylene and other non-polar 1-olefins has been commonly
25 accomplished using organometallic Ziegler-Natta
coordination-type catalysts, chromium catalysts, other
early transition metal catalysts as well as free-radical
type initiators. Although the array of catalysts
available provides different approaches to the
30 manufacture of polyolefins with differing physical and
mechanical properties, these catalysts are highly
susceptible to a range of substances which poison or
deactivate the catalyst's activity. It is well known
that even trace amounts of oxygen, carbon monoxide,
35 acetylene or water causes deactivation. Further,

catalyst deactivation is caused by organic compounds having oxygen donor groups such as ethers, esters, alcohols, or ketones. Industrial application of these organometallic catalysts requires careful and elaborate 5 measures to assure the absence of such poisons. Because these catalysts are easily poisoned, they tend to form low molecular weight materials, can not be used to provide copolymerization of ethylene with an oxygenated functional monomer, such as an ester, acid or ether 10 functionalized olefin, and generally may produce highly branched polymer products.

More recently, olefin polymerizaton catalysts have been developed which are less oxophilic than the early transition metal counterparts. For example, U.S. Patents 15 4,310,716; 4,382,153; 4,293,727; 4,301,318; and 4,293,502 each disclose late transition metal (e.g. Ni) complexes which provide low molecular weight oligomers of ethylene. Further, polymerization of ethylene has been successfully shown using complexes based on phosphorus ylide ligands 20 in Patent U.S. 4,537,982 as well as in U.S. Patents 4,698,403; 4,716,205; and 4,906,754. These nickel based catalysts formed from P-O bidentate ligands have been shown to provide high activity in the oligomerization and polymerization of ethylene. Still more recently, L. K. 25 Johnson et al in J. Am. Chem. Soc. 1995 117, 6414, reported the formation and use of Pd(II) and Ni(II) based cationic complexes formed from diimine ligands to provide high molecular weight polyolefins. Finally, WO 96/23010 describes a process for the polymerization of olefins 30 using a variety of transition metal complexes of certain diimine bidentate ligands. In many cases the polymerization provided highly branched polyolefins and were not shown to be useful in providing functionalized copolymer products. Further, in those instances where

functionalized copolymers were formed, it was shown that the functional groups reside exclusively at the end of chain branches.

5 Certain processes and cationic nickel (II) catalyst compositions have been described also by L.K. Johnson et al in WO 97/02298. These cationic complexes are described as active for the polymerization of ethylene and other olefins. They require use of an acid of a non-coordinating mono-anion, or some combination of compounds
10 that will generate such acid, in order for the catalyst composition to be rendered active towards olefin polymerization. The present neutral complexes, as well as the use of a Lewis base is not suggested by Johnson et al.

15 Löfgren et al, in Macromolecules 1997, 30, 171-175 describe polymerization of ethylene by cationic zirconium salen bis-chloride complexes with or without a Lewis base (tetrahydrofuran). They show that the catalyst composition exhibits only low levels of activity. There
20 are many references to the deleterious effect of Lewis base toward late transition metal catalyst compositions as well as single-site catalyst compositions of the metallocene type. For example, EP 94/304642 and EP 94/630910 disclose that Lewis base, such as dialkyl
25 ether, substantially terminates olefin polymerization by a single-site catalyst composition composed of a metallocene compound and partially hydrolyzed aluminum alkyl compound (aluminoxane). Additionally, U.S. 5,571,881 and WO 95/14048 indicate that an unsaturated
30 Lewis base, e.g., vinyl ether, either reacts with the cationic late transition metal catalysts to destroy their activity or causes reduction of the resultant polymer molecular weight. It is highly desired to provide a catalyst for the oligomerization and polymerization of

olefins, in particular ethylene, which provides a substantially linear (low degree of branching) product. It is also highly desired to provide a nonionic catalyst which can provide the linear polymer product. It is 5 still further desired to provide a nonionic catalyst which is capable of providing a product of high molecular weight which is substantially linear and, optionally, which is capable of promoting copolymerization of olefin and functionalized olefin monomer units.

10 Finally, it is desired to provide a catalyst composition composed of a non-ionic catalyst in combination with an adjunct agent and/or a Lewis base which is capable of providing a product of high molecular weight which is substantially linear and, optionally, 15 which is capable of promoting copolymerization of olefin and functionalized olefin monomer units.

Summary of the Invention

20 The present invention is directed to certain late transition metal pyrrolaldimine chelates as olefin oligomerization or polymerization catalysts, to the bidentate ligand compounds of substituted pyrrolaldimine which are precursors for said catalysts, to catalyst compositions composed of said pyrrolaldimine chelates in 25 combination with an adjunct agent and/or a Lewis base, the methods of forming said precursor compounds and said catalysts, and the method of polymerizing olefin monomers, especially ethylene, as well as copolymerization of olefin and functionalized olefin 30 monomers. Each of the above elements of the present invention is fully described herein below.

Detailed Description

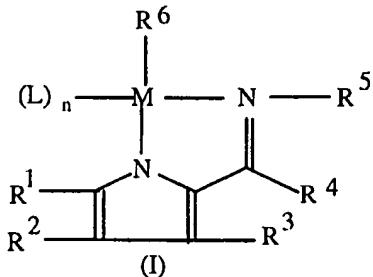
The present invention provides a process for polymerizing olefin monomers, in particular ethylene, in the presence of catalysts taken from the selected family 5 of pyrrolaldimine late transition metal chelates and to catalyst compositions composed of said pyrrolaldimine chelates in combination with an adjunct agent and/or a Lewis base, to produce olefin oligomers or polyolefins which can be either substantially linear and have a 10 weight average molecular weight of at least 150.

It has been presently found that certain 15 pyrrolaldimine late transition metal chelates can provide catalyst systems for the oligomerization or homopolymerization of ethylene and copolymerization of ethylene and functionalized olefins to provide substantially linear polymer products. The catalyst of the present invention can be represented by the following general formula:

20

25

30



wherein

R¹ represents a hydrogen atom, C₁-C₁₁ alkyl (preferably C₁-C₅, and most preferably tert-butyl); aryl, such as phenyl, biphenyl, terphenyl, naphthyl, anthracyl, phenanthracyl and the like; substituted aryl wherein the substitution group is selected from C₁-C₆ alkyl, perfluoroalkyl, nitro, sulfonate, or halo group; arylalkyl, such as toluyl and the like; halo, such as

chloro, bromo, and the like; nitro group; sulfonate group or siloxyl (-OSiA, where A is selected from phenyl or C₁-C₄ alkyl such as isopropyl or butyl and the like); or a hydrocarbyl terminated oxyhydrocarbylene group, -(BO)_zR⁷,
5 wherein each B independently represents a C₁-C₄ (preferably C₂-C₃) alkylene group or an arylene group (preferably phenyl, especially the B group adjacent to the base structure to which R¹ is bonded); R⁷ represents a C₁-C₁₁ (preferably a C₁-C₅) hydrocarbyl group such as an
10 alkyl or an unsubstituted or substituted aryl group, such as phenyl, biphenyl, naphthyl and the like, alone or substituted with one or more C₁-C₆ alkyl; and z is 1 to 4, R¹ is preferably a steric bulky group selected from aryl, substituted aryl or a branched C₃-C₆ alkyl group and most
15 preferably, phenyl, anthracyl, phenanthracyl, terphenyl or t-butyl:

20 R² represents hydrogen atom, aryl, substituted aryl, C₁-C₁₁ alkyl, halogen atom or R¹ and R² can, together provide a hydrocarbylene or substituted hydrocarbylene which forms a carbocyclic ring which may be non-aromatic or aromatic; R² is preferably hydrogen or, taken with R¹ as a carbocyclic ring group:

25 R³ represents hydrogen:

30 R⁴ represents hydrogen atom, a C₁-C₁₁ alkyl, an aryl group such as a phenyl or a substituted aryl group such as 2,6-dimethylphenyl or the like, and is preferably selected from hydrogen,

35 R⁵ represents a C₁-C₁₁ alkyl group (preferably a C₄-C₈ alkyl group) such as methyl, ethyl, propyl, t-butyl, and the like, a cycloalkyl group such as cyclohexyl and the like, an aryl group, such as phenyl, biphenyl, naphthyl or the like or a substituted aryl having one or both ortho positions of the aromatic group (especially the phenyl group) substituted with a C₁-C₄ alkyl and/or the

para position (with respect to the N-R⁵ bond) substituted with a hydrogen atom, nitro, trifluoromethyl, halogen atom, methoxy, or C₁-C₄ alkyl or fused or unfused aryl, sulfonate, or a hydrocarbyl terminated oxyhydrocarbylene group, -(BO)_nR' as defined in R' above. R⁵ is preferably a t-butyl or a cycloalkyl such as adamantyl, or a 2,6-di(C₁-C₄ alkyl)phenyl group and most preferably 2,6-diisopropyl phenyl or 2,6-diisopropyl-4-nitrophenyl:

R¹ and R⁵ can, together, form an oxyhydrocarbylene chain, e.g., -(BO)_mB- wherein each B independently represents a C₁-C₄ alkylene group or an arylene group and m is an integer of from 2 to 5 preferably 3-5;

n is an integer of 0 or 1;

R⁶ represents, when n is 1, an unsubstituted or substituted aromatic group, such as phenyl which is preferably unsubstituted, a C₁-C₁₁ alkyl (preferably a C₁-C₅ alkyl and most preferably methyl), a hydrogen atom or halogen atom (preferably chloro or bromo), or when n is 0, R⁶ represents an allyl or substituted allyl group wherein the substitution can be selected from a halogen atom, a nitro group or a sulfonate group:

L represents a coordination ligand such as triphenylphosphine, tri(C₁-C₆ alkyl) phosphine, tricycloalkyl phosphine, diphenyl alkyl phosphine, dialkyl phenylphosphine, trialkylamine, arylamine such as pyridine, C₂-C₂₀ alkene such as octene, decene, dodecene, alkyl and the like, a substituted alkene wherein the substitution group may be selected from a halogen atom (preferably chloro), an ester group, a C₁-C₄ alkoxy group, an amine group (-NR₂ wherein each R is hydrogen, or a C₁-C₄ alkyl), carboxylic acid or its alkali metal salt, di(C₁-C₄)alkyl ether, tetrahydrofuran, a nitrile such as acetonitrile and the like:

M represents one of the transition metals, that is a Group VIII or Group IV transition metal selected from Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt in the +2 oxidation state or Ti, Zr, Hf in the +4 oxidation state and preferably a late transition metal selected from iron, cobalt, nickel or palladium and most preferably either nickel or palladium.

The present invention provides a catalyst which contains sterically bulky groups both above and below as well as within the plane of orientation with respect to the transition metal of the complex. It is believed, though not meant to be a limitation of the invention, that the steric and electronic configuration of the presently achieved complex provides the following desired characteristics:

- (1) it utilizes late transition metals (preferably Ni or Pd) to provide high resistance to deactivation by oxygenated species;
- (2) it contains certain bidentate, chelating ligand groups which are believed to enhance the selectivity-controlling effect in the polymerization of ethylene and of α -olefins;
- (3) it contains groups of extreme steric bulk which provide shielding or partial shielding of the axial faces of the transition metal (II) square planar complexes and thereby it is believed, retards associative displacement and chain transfer during the polymerization; and
- (4) the steric bulk which is within the plane of the transition metal (II) square planar complex may inhibit chain migration processes and thereby cause substantially linear polymerization.

- (5) the steric bulk which is within the plane of the transition metal (II) square planar complex may promote dissociation of the ancillary ligand, L, and

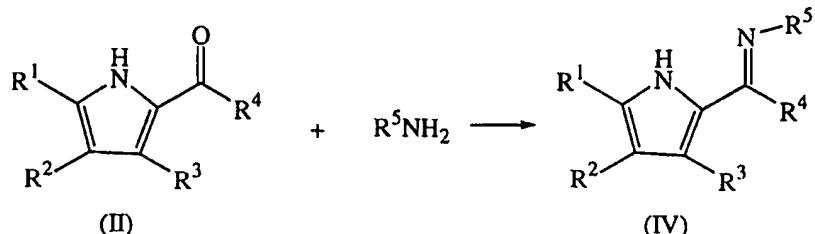
thereby result in an increase in the number of active polymerization sites.

The catalysts (I) are most preferably those having bulky substituents, such as aryl as, for example, 5 anthracenyl, phenanthracenyl, or terphenyl and the like, and substituted aryl groups such as 2,6-diisopropylphenyl and the like, in the R¹ and/or R⁵ positions. The substitution group may be a C₁-C₄ alkyl and/or an electron withdrawing group such as NO₂, halogen, sulfonate (SO₃⁻), 10 sulfonyl ester (SO₂R), carboxyl (COO⁻), or perfluoroalkyl group.

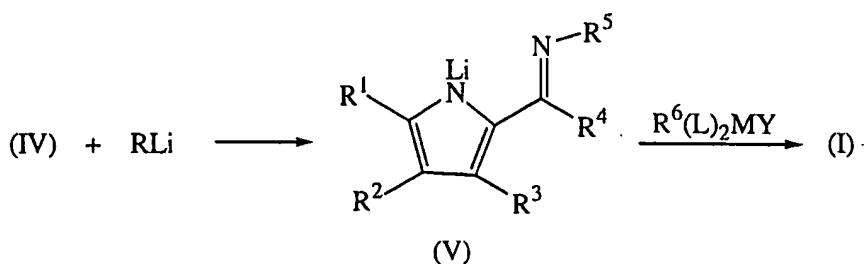
The catalyst (I) of the present invention may further contain an ether or polyether group as part of structure of the subject pyrrolaldimine. The incorporation of such group(s) can be made at R¹ and/or at 15 R⁵ or as an oxyhydrocarbylene chain between R¹ and R⁵ such that a hydrocarbon moiety of said oxyhydrocarbylene is directly bonded to the nitrogen atom at R⁵ and to the ring at R¹. Such catalysts provide enhanced catalytic 20 activity over catalyst (I) absent said group(s) and do not require the use of adjunct agent or Lewis base additive, as described herein below.

Synthesis of the precursor ligands can be achieved by reacting the appropriate pyrrole-2-carboxaldehyde 25 (having desired substituent groups on the pyrrole ring) with a primary amine (R⁵NH₂), such as 2,6-diisopropylaniline and the like. The reaction can be carried out in solution with an inert solvent, such as a C₁-C₅ alcohol (e.g. methanol, ethanol or the like) or 30 aromatic compound (e.g., benzene, toluene or the like). The reaction is preferably carried out at temperatures of from about 15°C to 80°C (most preferably at from 15 to 25°C) for a period of from one to twenty hours (most preferably from 10 to 12 hours). The reaction is carried

out at atmospheric pressure and in the presence of a catalytic amount of an organic acid, such as toluenesulfonic acid to provide the pyrrole-2-carboxaldehyde ligand (IV) according to the equation below:



The bidentate ligand (IV) can be deprotonated using a strong alkali metal alkyl, such as a lithium alkyl (e.g., n-butyl Li) to form the alkali metal (e.g., lithium) salt (V). The deprotonation is carried out at low temperatures such as about 0° to 30°C (preferably 0° to 10°C) at normal atmospheric pressure and in the presence of an inert solvent, such as tetrahydrofuran, dialkyl ether, C₅-C₁₀ hydrocarbon, dioxane and the like. The reaction normally is completed in a short period, such as from about 5 to 30 minutes. The lithium salt (V) can then be reacted with a late transition metal coordination compound of the type R⁶(L)₂MY, wherein each R⁶ and L are as defined above, and Y represents a halogen atom, as for example bis(triphenylphosphine) phenyl nickel chloride, and the like. This reaction may be conducted in an inert solvent, such as tetrahydrofuran, dialkyl ether, C₅-C₁₀ hydrocarbon, and the like at temperatures of from about 10 to 90°C (preferably 10° to 30°C) for periods of from one to fifteen hours (normally 10-15 hours) to provide catalyst (I) as follows:



In the above, the R¹ may be hydrogen but preferably is a bulky group which provides a steric shield of the transition metal's equatorial face by being well-positioned in the plane of the transition metal complex as well as some bulk in the axial face. For example, R¹ is preferably an aryl, such as phenyl, biphenyl, terphenyl, naphthyl, anthracenyl, or phenanthracenyl, a nitro-substituted aryl, or a bulky alkyl, such as a tert-butyl group. Such substituted pyrrole carboxaldehydes (II) are readily formed by formylation of an appropriately substituted pyrrole. This is conventionally accomplished by reacting the substituted pyrrole with an aldehyde source, such as formaldehyde (e.g., paraformaldehyde, 1,3,5-trioxane) in the presence of stannous chloride catalyst according to the procedures described by Casirighi et al in J. Chem. Soc. Perkins Trans. I, 1980, 1862-5, the teachings of which are incorporated herein by reference in its entirety.

As indicated above, R¹ may be selected from sterically bulky groups other than hydrocarbyl groups as, for example, siloxane groups. Such substitution can be readily accomplished by using a 5-hydroxy-2-carboxaldehyde pyrrole as the starting material II to form the Schiff base aldimine compound IV. The hydroxyl group can then be converted to a siloxy group by reaction with the appropriate aryl, alkyl or mixed substituted silyl halide as, for example triisopropyl silyl chloride,

diphenyl-t-butyl silyl chloride, triphenyl silyl chloride and the like. Deprotonation and reaction with transition metal coordination compound of the type $R^6(L)_2, MY$ provides the desired catalyst compound I in the manner described above.

As defined above, R^1 and R^5 may each independently be selected from a hydrocarbyl terminated oxyhydrocarbylene containing group. Such groups may be represented as $-(BO)_zR'$ wherein each B is independently selected from a C_1-C_4 (preferably a C_2-C_3) alkylene group or an arylene group and R' represents a C_1-C_{11} (preferably C_1-C_5) hydrocarbyl group such as alkyl, an aryl, an alkaryl, or an aralkyl group and z represents an integer of 1 to 4. Such oxyhydrocarbylene group may be made part of compound I by mono-alkylation of 2-(2-hydroxyphenyl)-pyrrole or the N-protected 2-hydrophenylpyrrole with bromoethyl ether, followed by formylation of the pyrrole ring adjacent to the nitrogen, followed by imine formation and finally metallation with $R^6(L)_2, MY$ in the manner described previously.

It has been found that substituted pyrrolaldimine complexes (I) of late transition metals described above provide a catalytic composition having catalytic activity for olefin (e.g., ethylene) oligomerization or polymerization and provide substantially linear product having a low degree of branching. These complexes are neutral compounds and, as such do not require the presence of organo aluminum or hydrolyzed organo aluminum compounds or other reducing agent to cause activation of the complex towards olefin insertion reaction and polymerization. However, organo aluminum and hydrolyzed organo aluminum compounds, such as methyl alumoxane or trialkyl aluminum compounds and the like, may be present

and are preferably present when R⁶ is halogen. Compounds I are a new family of complexes of single-site catalysts.

The subject catalysts (I) may be used as the sole catalyst component of the catalyst composition (this is especially acceptable when the bulky group R¹ is large such as phenyl, biphenyl, terphenyl, anthracenyl, phenanthracenyl, nitro-substituted aryl or the like) or may be used in combination with an adjunct agent and/or a Lewis base. The adjunct agent comprises known phosphine sponge material capable of facilitating phosphine (ligand L) dissociation and trapping of free phosphine. Such catalyst composition adjunct agents are, for example, bis(cyclooctadiene)-nickel, tris(pentafluorophenyl) boron, 9-borabicyclo[3.3.1]nonane (9-BBN), methyl iodide and the like.

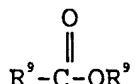
It has unexpectedly been found that the subject catalyst provides an enhanced catalyst composition when combined with a Lewis base as, for example ethers, esters, aldehydes, ketones, alcohols, amides, organo carbonates, organonitro compounds, or mixtures thereof and even water. It is commonly believed that organometallic catalysts should be combined with Lewis acid compounds to provide effective catalyst systems and that water acts as a poison to such catalysts. In contrast to the present unexpected finding, it has been previously deemed important to use conventional single site catalysts, such as metallocene catalysts, in the absence of moisture or other oxygenated compounds in order to provide an effective catalyst system.

The Lewis base additives found useful in forming a catalyst composition with the catalyst of compound I or V comprise ether compounds, such as dialkyl ethers where each alkyl group is independently selected from a C₁-C₁₈ alkyl, preferably a C₁-C₆ alkyl group as, for example,

diethyl ether, methyl ethyl ether, diisopropyl ether, ethyl propyl ether, dibutyl ether and the like; vinyl ethers such as ethyl vinyl ether and the like; aryl ethers as, for example, dibenzyl ether, diphenyl ether, 5 dinaphthyl ether and the like, mixed ethers as, for example, amyl phenyl ether, methyl benzohydryl ether, benzyl phenyl ether, anisole, phenetole and the like. The ether additive may also be selected from cyclic ethers as, for example, tetrahydrofuran, dioxane-1,4, 10 dioxane-1,3, crown ethers such as 18-crown-6, 14-crown-5, 12-crown-4 and the like as well as polyethers such as dimethyoxyethane, diglyme, triglyme, pentaglyme or polyoxyalkylenes as, for example, polyoxyethylene (preferably lower molecular weight polymers which are 15 miscible in the polymerization solvent used).

The above ethers, especially the alkyl and/or aryl group containing ethers and cyclic ethers described above, and most preferably dialkyl ether (e.g., diethyl ether) and low molecular weight polyethers (e.g., 20 dimethyoxyethane) have been found to be effective solvents or co-solvents for use in the polymerization process when the subject catalyst of compound I or compound V is used, as described herein below.

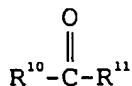
The Lewis base may be selected from an organic ester 25 represented by the formula



30 wherein each R' is independently selected from a C₁-C₁₁ alkyl group, preferably a C₁-C₅ alkyl group as, for example, ethyl acetate, propyl acetate, hexyl acetate, ethyl butyrate, propyl butyrate, ethyl caproate, ethyl 35 caprylate, ethyl laurate and the like.

Further, aldehydes and ketones have been found useful as a Lewis base additive in forming the subject catalyst composition. They may be represented by the formula

5

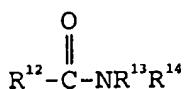


10 wherein R¹⁰ represents a C₁-C₁₂ hydrocarbyl selected from unsubstituted or substituted (e.g., carbonyl) alkyl, aryl, alkaryl or aralkyl groups and R¹¹ represents a hydrogen atom or an R¹⁰ group, which is independently selected. For example, the aldehyde or ketone may be
 15 selected from acetone, propanone, butyronone, 4-heptanone, 2,4-pentanedione and the like, as well as cyclic ketones such as cyclohexanone, 1,4-cyclohexanedione and the like, or an aldehyde such as acetaldehyde, capraldehyde, valeraldehyde and the like.

20 Still further, an alcohol can be used as the Lewis base additive in forming the subject catalyst composition. They may be selected from monohydric or polyhydric alcohols including, for example, alcohols having hydrocarbyl moiety composed of a C₁-C₁₂ (preferably C₁-C₃) alkyl, aryl (e.g., phenyl or benzyl), alkaryl and aralkyl groups. Examples of such alcohols include methanol, ethanol, propanol, isopropanol, butanol, t-butanol, 2-pentanol, 3-hexanol, glycol, 1,2,3-propanetriol, phenol, phenethyl alcohol, para-methyl
 25 phenol and the like.

30 35 Amides can be used as the Lewis base additive in forming the subject catalyst composition. The amides may be represented by the formula

35



wherein R¹² and R¹³ each independently represent a C₁-C₁₁ hydrocarbyl, R¹⁴ represents hydrogen or a C₁-C₁₁ hydrocarbyl. R¹³ and R¹⁴ are, preferably, independently selected from a C₁-C₅ alkyl group.

Nitroalkanes and nitroaromatics have also been found to be useful as a Lewis base additive in forming the subject catalyst composition. The nitroalkanes may be a mono (preferred) or poly nitro compound formed with a C₁-C₁₁ (preferably a C₁-C₅) alkyl group. The aromatic nitro should be a mono nitro compound such as nitrobenzene and the like.

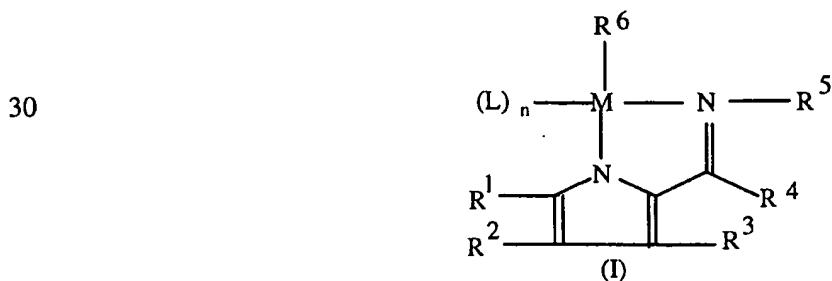
It has been unexpectedly found that the subject catalyst composition may contain small amounts of water and that the presence of water does not destroy the activity of the catalyst of the subject invention. Thus, unlike most organometallic catalysts useful in olefin polymerization, the presently described catalyst can be used in the presence of small amounts of moisture to provide a catalyst composition which can remain active in the polymerization or oligomerization of olefins or mixtures of olefins and a functional olefin monomer(s).

The amount of the Lewis base (except water) additive can be substantially any amount desired with from 10⁰ to 25 10⁴ times the amount of compound I or V on a molar base being preferred and, most preferred, from 10¹ to 10³ times the molar amount of catalyst when ether is the Lewis base used and from 10⁰ to 10² times the molar amount of catalyst with respect to other Lewis bases. In the case 30 of water, the molar ratio of water to catalyst can range from 0 to about 10², preferably, from 0 to 10¹.

This invention concerns processes for making polymers, comprising, contacting the subject catalyst composition with one or more selected olefins or

cycloolefins, alone or optionally with a functional α -olefin such as a carboxylic acid of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{COOH}$, a carboxylic acid ester of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}'$ or $\text{CH}_2=\text{CHCOR}'$, an alkyl vinyl ether of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{OR}'$, vinyl ketones of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{C(O)R}'$, a vinyl alcohol of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{OH}$, or a vinyl amine of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{NR}^8_2$, wherein m is an integer of 0 to 10 and R' is a $\text{C}_1\text{-C}_{10}$ hydrocarbyl group, aryl or substituted aryl group (preferably methyl) and R^8 is independently selected from hydrogen or an R' group; a functional cycloolefin, such as functionalized norbornene wherein the functional group is an ester, alcohol, carboxylic acid, halogen atom, primary, secondary or tertiary amine group or the like; or unsaturated dicarboxylic acid anhydride or carbon monoxide or the like and other selected monomers, such as vinyl halides. The subject catalyst composition is composed of the subject transition metal containing compound (I) described above or a combination of compound (V) and transition metal complex, as described herein below. The "polymerization process" described herein (and the polymers made therein) is defined as a process which produces a polymer or oligomer with a weight average molecular weight (M_w) of at least about 150, preferably at about 1000.

The subject catalysts may generally be written as



wherein each symbol R¹, R², R³, R⁴, R⁵, R⁶, L, and M are defined above. Preferably M is Ni(II) or Pd(II).

Alternately, the catalytic polymerization of the present invention can be carried by contacting one or more selected olefins or cycloolefins alone or optionally with a functional olefin monomer, as described above with a catalyst composition composed of one or more bidentate ligand (V) described above in combination with a transition metal (M) organic complex. The ligand (V) and complex should be used in about a 1:1 molar ratio. In a preferred embodiment of the present invention, the bidentate ligand V is combined with a transition metal organic complex of the formula R⁶(L)₂MY in about a 1:1 molar ratio in the presence of olefin and/or cycloolefin alone or optionally with a functional olefin monomer. The catalyst composition composed of ligand (V) and transition metal organic complex may further contain a phosphine sponge and/or Lewis base additive, such as those described above, or an organo aluminum or hydrolyzed organo aluminum compound or mixtures thereof as described above with respect to catalyst compositions composed of compound (I) which have a halogen as R⁶.

In all catalysts and precursor bidentate ligands, described herein, it is preferred that R¹ and R⁵ are each independently a sterically bulky hydrocarbyl. In one form it is especially preferred that R¹ and R⁵ are each independently aryl or substituted aryl groups. In another form, it is preferred that R¹ and/or R⁵ be independently selected from a hydrocarbyl terminated oxyhydrocarbylene containing group, as described above. It is preferred that when R⁵ is a substituted aryl the 4 position of the aryl (with respect to the N-bond) be either hydrogen or nitro.

When using I or V as a catalyst, it is preferred that R², R³ and R⁴ are hydrogen or methyl, unless R² is, when taken together with R¹, a C₄-C₁₀ carbocyclic group which may or may not be aromatic. It is also preferred
5 that either or both R¹ and R⁵ are biphenyl, terphenyl, anthracenyl, phenanthracenyl, 2,6-diisopropylphenyl, 2,6-dimethylphenyl, 2,6-diethylphenyl, 4-methylphenyl, 2-isopropyl-6-methylphenyl, phenyl, 2,4,6-trimethylphenyl, 2-t-butylphenyl, 2-t-butyl-6-methylphenyl, 2,6-diisopropyl-4-nitrophenyl, and 10-nitroanthracenyl.
10

The structure of the ligand associated with compound I or compound V may influence the polymer microstructure and polymer molecular weight. For example, it is preferred that R¹ be a bulky aryl or substituted aryl group. Complexes with R¹ of this type generally produce
15 higher molecular weight and more linear polymer product for any given set of conditions.

The catalyst or catalyst composition of I or V with the phosphine sponge adjunct or organo aluminum compound
20 adjunct or with the Lewis base additive or mixtures of adjunct and Lewis base, when optionally used, are contacted, usually in a liquid phase, with ethylene or other alpha-olefin (RCH=CH₂), and/or 4-vinylcyclohexane, 4-vinylcyclohexene, cyclopentene, cyclobutene,
25 substituted norbornene, or norbornene. The liquid phase may include a compound added just as a solvent and/or may include the monomer(s) itself and/or may comprise the Lewis base (especially an ether compound) in the liquid phase at reaction conditions. When an adjunct is used,
30 the molar ratio of adjunct to compound I or V is from about 0.001:1 to 15:1, preferably about 0.01:1 to about 8:1 and most preferably from 0.1:1 to 3:1. The temperature at which the polymerization is carried out is from about -100°C to about +200°C, preferably about -20°C

to about +100°C and most preferably between about 0°C and 90°C. All ranges of temperatures between -100 and +200°C being covered by this teaching. The pressure at which the polymerization is carried out is not critical, 5 atmospheric pressure to about 100 MPa, or more, being a suitable range. The pressure may affect the yield, molecular weight and linearity of the polyolefin produced, with increased pressure providing higher molecular weight, more linear oligomer or polymer product.

10 Preferred alpha-olefins and cyclic olefins in the polymerization are one or more of ethylene, propylene, 1-butene, 2-butene, 1-hexene, 1-octene, 1-pentene, 1-tetradecene, norbornene, and cyclopentene, with ethylene, 15 propylene, cyclopentene and norbornene being more preferred. Ethylene (alone as a monomer) is especially preferred.

20 The polymerization may be run in the presence of various liquids. The solvent in which the polymerization may be conducted can be selected from (i) the monomer(s), per se or (ii) any organic compound which is liquid under the reaction conditions and is substantially inert to the reactants and product, or (iii) a Lewis base additive (except water which, when used, should be present in 25 limited amounts) which is liquid under the reaction conditions, or mixtures thereof. Particularly preferred are aprotic organic liquids or organic ethers or mixtures thereof. The catalyst system, monomer(s), and polymer may be soluble or insoluble in these liquids, but 30 obviously these liquids should not prevent the polymerization from occurring. Suitable liquids include alkanes, cycloalkanes, halogenated hydrocarbons, ethers, halogenated aromatic hydrocarbons and aromatic hydrocarbons. Specific useful solvents include hexane,

heptane, toluene, xylenes, benzene, methylene chloride, ethyl ether, dimethoxyethane, tetrahydrofuran and crown ethers.

The catalyst compositions of the present invention cause polymerization of one or more alpha-olefin, with functional olefins such as those described herein above. When carbon monoxide is used as a comonomer, it forms alternating copolymers with the various alpha-olefins. The polymerization to form the alternating copolymers is carried out with both CO and the olefin simultaneously present in the process mixture, and in the presence of the present catalyst composition.

The catalyst of the present invention may also be supported on a solid material (as opposed to just being added as a suspended solid or in solution), for instance on silica gel, zeolites, crosslinked organic polymers, such as styrene-divinylbenzene copolymer and the likes thereof. By supported is meant that the catalyst may simply be carried physically on the surface of the solid support, may be adsorbed, or may be carried by the support by other means.

In many of the polymerizations, certain general trends may occur, although for all of these trends there are exceptions. Pressure of the monomers (especially gaseous monomers such as ethylene) has an effect on the polymerizations in many instances. Higher pressure often reduces branching and extends polymer chain length, especially in ethylene containing polymers. Temperature also affects these polymerizations. Higher temperature usually increases branching.

In general, the period of time during which the catalyst of compound I or the catalyst composition formed from compound V, remains active is influenced by the particular ligand structure, polymerization temperature,

or type of Lewis base present. Catalyst lifetime is long when Lewis base such as ether is present, co-catalyst adjunct is absent, and R¹ is a bulky aryl or substituted aryl group.

5 When the polymer product of the present invention is a copolymer of functionalized group containing monomer, the functional group may be further used to cross-link the polymer. For example, when copolymers of an olefinic carboxylic acid or olefinic ester and an alpha-olefin are
10 made, they may be crosslinked by various methods known in the art, depending on the specific monomers used to make the polymer. For instance, carboxyl or ester containing polymers may be crosslinked by reaction with diamines or with diisocyanates to form bisamides. The carboxyl
15 groups may also be neutralized with a monovalent or divalent metal containing base (e.g., NaOH, CaO) to form ionomeric or pseudo-crosslinked polyolefin copolymer.

The resultant polymers formed according to the present invention, especially those of ethylene homo or copolymers may have varying degrees of branching in the polymer. Branching may be determined by NMR spectroscopy (see the Examples for details), and this analysis can determine the total number of branches, the branching distribution and to some extent the length of the
25 branches. Herein the amount of branching is expressed as the number of branches per 1000 of the total methylene (-CH₂-) groups in the polymers, with one exception. Methylene groups that are in an ester grouping, i.e., -CO₂R; a ketone group, i.e., -C(O)R are not counted as part
30 of the 1000 methylenes. The polymers formed with the aid of the present catalyst have low branching of from about 10 to 150 branches per 1000, and normally from about 20 to 120 branches per 1000, for example, ethylene homopolymers have a branch content of about 0 to about

150 branches per 1000 methylene groups, preferably about 5 to about 100 and most preferably about 3 to about 70 branches per 1000 methylene groups. These branches do not include polymer end groups.

5 The polymers formed by the present invention may be mixed with various additives normally added to elastomers and thermoplastics [see EPSE (below), vol. 14, p. 327-410] which teaching is incorporated herein by reference. For instance reinforcing, non-reinforcing and conductive
10 fillers, such as carbon black, glass fiber, minerals such as silica, clay, mica and talc, glass spheres, barium sulfate, zinc oxide, carbon fiber, and aramid fiber or fibrils, may be used. Antioxidants, antiozonants, pigments, dyes, slip agents, antifog agents, antiblock
15 agents, delusterants, or compounds to promote crosslinking may be added. Plasticizers such as various hydrocarbon oils may also be used.

20 The polymers formed by the present invention may be used for one or more of the applications listed below.
25 In some cases a reference is given which discusses such uses for polymers in general. All of these references are hereby included by reference. For the references, "U" refers to W. Gerhartz, et al., Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed. VCH Verlagsgesellschaft mbH, Weinheim, for which the volume and page number are given, "ECT3" refers to the H. F. Mark, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, "ECT4" refers to the J. I. Kroschwitz, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, for which the volume and page number are given. "EPST" refers to H. F. Mark, et al., Ed., Encyclopedia of Polymer Science and Technology, 1st Ed., John Wiley & Sons, New York, for which the volume and

page number are given, "EPSE" refers to H. F. Mark, et al., Ed., Encyclopedia of Polymer Science and Engineering, 2nd Ed., John Wiley & Sons, New York, for which volume and page numbers are given, and "PM" refers to J. A. Brydson, ed., Plastics Materials, 5th Ed., Butterworth-Heinemann, Oxford, UK, 1989, and the page is given. In these uses, a polyethylene, polypropylene and a copolymer of ethylene and propylene are preferred.

1. The polyolefins herein are especially useful in blown film applications because of their particular rheological properties (EPSE, vol. 7, p. 88-106). It is preferred that these polymers have some crystallinity.

2. The polymers are useful for blown or cast films or as sheet (see EPSE, vol. 7 p. 88-106; ECT4, vol. 11, p 843-856; PM, p. 252 and p. 432ff). The films may be single layer or multilayer, the multilayer films may include other polymers, adhesives, etc. For packaging the films may be stretch-wrap, shrink-wrap or cling wrap and may be heat sealable. The films are useful for many applications such as packaging foods or liquids, geomembranes and pond liners. It is preferred that these polymers have some crystallinity.

3. Extruded films or coextruded films may be formed from these polymers, and these films may be treated, for example by uniaxial or biaxial orientation after crosslinking by actinic radiation, especially electron beam irradiation. Such extruded films are useful for packaging of various sorts. The extruded films may also be laminated to other films using procedures known to those skilled in the art. The laminated films are also useful for packaging of various sorts.

4. The polymers, particularly the elastomers, may be used as tougheners for other polyolefins such as polypropylene and polyethylene.

5. Tackifiers for low strength adhesives (U, vol. A1, p 235-236) are a use for these polymers. Elastomers and/or relatively low molecular weight polymers are preferred.

6. An oil additive for smoke suppression in single-stroke gasoline engines is another use.

10 Elastomeric polymers are preferred.

7. The polymers are useful as base resins for hot melt adhesives (U, vol. A1, p 233-234), pressure sensitive adhesives (U, vol. A1, p 235-236) or solvent applied adhesives. Thermoplastics are preferred for hot melt adhesives.

8. Base polymer for caulking of various kinds is another use. An elastomer is preferred. Lower molecular weight polymers are often used.

9. Wire insulation and jacketing may be made from any of the polyolefins (see EPSE, vol. 17, p. 828-842). In the case of elastomers it may be preferable to crosslink the polymer after the insulation or jacketing is formed, for example by free radicals.

25 The following examples are provided herein below for illustrative purposes only and are not meant to be a limitation on the scope of the invention. All parts and percentages are by weight unless otherwise indicated.

Example I

30 $C_4H_3N(H)-2-C(H)=N-2,6-C_6H_3(i-Pr)_2$

To a benzene (50 mL) solution of 2-pyrrolecarboxaldehyde (5.0 g, 54 mmol) was added 2,6-diisopropylaniline (12 g, 70 mmol) and *p*-toluenesulfonic acid (40 mg). The reaction was stirred under reflux for

24 hours. After this time, the solution was concentrated under vacuum to yield a red-brown oil. Methanol (30 mL) was added to the oil which resulted in precipitation of a white solid. The solid was isolated by filtration through a glass frit and washed with additional methanol to yield 6.8 g (50%) of a white solid. ^1H NMR (C_6D_6): δ 1.10 (d, 12H, $J_{\text{HH}}=6.90$ Hz), 3.06 (septet, 2H, $J_{\text{HH}}=6.90$ Hz), 6.17 (br s, 1H), 6.40 (t, 1H, $J_{\text{HH}}=2.54$ Hz), 6.61 (d, 1H, $J_{\text{HH}}=2.54$ Hz), 7.10-7.18 (m, 3H), 7.95 (s, 1H); ^{13}C NMR (C_6D_6): δ 23.6, 27.9, 109.8, 116.7, 123.2, 124.2, 124.5, 129.8, 139.0, 148.4, 152.7.

Example II

[$\text{C}_4\text{H}_3\text{N}-2-\text{C}(\text{H})=\text{N}-2,6-\text{C}_6\text{H}_3(\text{i-Pr})_2$] Nickel(phenyl)(PPh₃)

In a Schlenk flask was dissolved the Li salt of the product from Example I (0.24 g, 0.72 mmol) and bis(triphenylphosphine)nickel(phenyl)chloride (0.50 g, 0.73 mmol) in Et₂O (20 mL). The reaction was stirred at room temperature for 1 hour. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added and the reaction was cooled to -78°C. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.35 g (74.0%) of a yellow-orange solid. ^1H NMR (C_6D_6): δ 1.11 (d, 6H, $J_{\text{HH}}=6.77$ Hz), 1.30 (d, 6H, $J_{\text{HH}} = 6.77$ Hz), 3.96 (septet, 2H, $J_{\text{HH}} = 6.77$ Hz), 6.17 (br s, 1H), 6.40 (t, 1H, $J_{\text{HH}} = 2.54$ Hz), 6.61 (d, 1H, $J_{\text{HH}} = 2.54$ Hz), 5.96-7.65 (m, 26H); ^{13}C NMR (C_6D_6): δ 22.6, 26.1, 28.9, 113.3, 117.9, 121.6, 122.6, 125.8, 125.9, 130.0, 130.1, 132.1, 132.7, 134.8 (d, $J_{\text{CP}} = 10.8$ Hz), 136.8, 140.3, 141.3, 142.4, 146.5, 162.3; ^{31}P NMR (C_6D_6): δ 33.10. Anal. Calcd for $\text{C}_{41}\text{H}_{41}\text{N}_2\text{NiP}$:

C, 75.59; H, 6.34; N, 4.30. Found: C, 75.74; H, 6.41; N, 4.15.

Example III

5 1.8 mM of the catalyst product formed in Example II above was weighed out and introduced into a pressure container under an atmosphere of nitrogen. The container was evacuated and backfilled with ethylene. 80 mL of dry toluene was then cannula transferred into the pressure
10 container. 5 mL of toluene solution containing 2 meq. of a phosphine sponge adjunct, bis(cyclooctadiene)-nickel was syringed into the container. Additional ethylene was introduced to raise the pressure to 80 psi at 25°C. The reaction was allowed to proceed with stirring for 40
15 minutes. After completion of the polymerization, methanol (500 mL) was introduced to terminate the reaction. No precipitate was recovered. The reaction solution was analyzed by gas chromatography using standard analytical techniques. The reaction mixture was
20 found to contain a mixture of C₁₂-C₁₂ hydrocarbons.

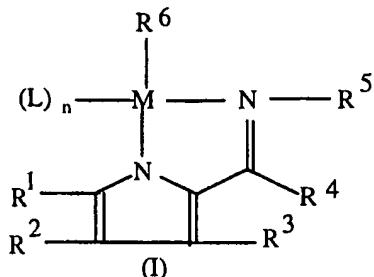
IN THE CLAIMS:

1. A compound represented by the formula:

5

10

15



wherein

R¹ represents a hydrogen atom; C₁-C₁₁ alkyl; aryl; substituted aryl wherein the substitution group is selected from C₁-C₄ alkyl, perfluoroalkyl, nitro, sulfonate or halo group; arylalkyl; siloxyl (-OSiA, where A is selected from phenyl or C₁-C₄ alkyl); nitro group; sulfonate group; halo atom; or a hydrocarbyl terminated oxyhydrocarbylene group (-(BO)_zR⁷), wherein each B independently is selected from a C₁-C₄ alkylene or an arylene group, O represents oxygen, R⁷ represents a C₁-C₁₁ hydrocarbyl group and z is an integer of 1 to 4;

R² represents hydrogen atom; aryl; substituted aryl, C₁-C₁₁ alkyl; halogen atom; or R¹ and R², together, provide a hydrocarbylene or substituted hydrocarbylene which forms an aromatic or non-aromatic carbocyclic ring;

R³ represents hydrogen;

R⁴ represents hydrogen atom; a C₁-C₁₁ alkyl; an aryl; substituted aryl group; or R³ and R⁴, together, provide a hydrocarbylene or substituted hydrocarbylene forming a non-aromatic carbocyclic ring;

R⁵ represents a C₁-C₁₁ alkyl; C₅-C₆ cycloalkyl; aryl group; a substituted aryl having one or both ortho positions of the aromatic group substituted with a C₁-C₄ alkyl, the para position (with respect to the N-R⁵ bond) substituted with a hydrogen, nitro, trifluoromethyl, halogen, methoxy, C₁-C₄ alkyl, sulfonate or fused or unfused aryl group; or a hydrocarbyl terminated oxyhydrocarbylene group -(BO)₂R⁷); or R¹ and R⁵ together form an oxyhydrocarbylene chain, -(BO)_mB-, wherein each B is independently selected from a C₁-C₄ alkylene or an arylene group and m is an integer of 1-4;

n represents an integer of 0 or 1;

R⁶ represents, when n is 1, an unsubstituted or substituted aromatic group; a C₁-C₁₁ alkyl; a hydrogen atom or halogen atom or, when, n is 0, R⁶ represents an allyl group or substituted allyl group;

L represents a coordination ligand selected from triphenylphosphine, tri(C₁-C₆ alkyl) phosphine tricycloalkyl phosphine, diphenyl alkyl phosphine, dialkyl phenylphosphine, triphenoxyphosphine, trialkylamine, pyridine, C₂-C₂₀ alkene, substituted C₂-C₅ alkene, C₁-C₄ alkoxy, di(C₁-C₆ alkyl) ether, tetrahydrofuran, or a nitrile; and

M represents a Group IV or VIII transition metal selected from Ti, Zr, Hf in the +4 oxidation state or Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt in the +2 oxidation state.

2. The compound of Claim 1 wherein R¹ is selected from aryl, substituted aryl or C₁-C₆ alkyl group.

3. The compound of Claim 1 wherein R⁵ is selected from aryl or substituted aryl, alkyl or cycloalkyl.

4. The compound of Claim 2 wherein R⁵ is selected from aryl or substituted aryl.

5. The compound of Claim 2 wherein R⁵ is selected from alkyl or cycloalkyl.

6. The compound of Claim 1 wherein R¹ is t-butyl and R⁵ is a 2,6-di(C₁-C₅ alkyl)phenyl.

10 7. The compound of Claim 1, 2, 3, 4, 5, or 6 wherein M is nickel atom or palladium atom.

8. The compound of Claim 1 wherein R¹ is selected from t-butyl, anthracenyl or phenanthracenyl.

15 9. The compound of Claim 2 or 8 wherein R⁵ is 2,6-di(C₁-C₅ alkyl)phenyl group.

20 10. The compound of Claim 9 wherein R⁵ is 2,6-di(isopropyl)phenyl.

11. The compound of Claim 1 wherein R¹ is selected from a hydrocarbyl terminated oxyalkylene group represented by the formula -(BO)_zR' wherein B is a C₁-C₄ alkylene, O is oxygen, R' is a C₁-C₁₁ hydrocarbyl and z is 1-4.

30 12. The compound of Claim 1 wherein R⁵ is selected from an aryl group substituted with a hydrocarbyl terminated oxyalkylene group represented by the formula -(BO)_zR' wherein B is a C₁-C₄ alkylene, O is oxygen, R' is a C₁-C₁₁ hydrocarbyl and z is 1-4.

13. The compound of Claim 1 wherein R⁵ is selected from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is anthracenyl.

14. The compound of Claim 1 wherein R⁵ is selected
5 from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is phenanthracenyl.

15. The compound of Claim 1 wherein R⁵ is selected from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is phenyl.
10

16. The compound of Claim 1 wherein R¹ and R⁵ together represent a polyoxyhydrocarbylene group.

17. The compound of Claim 13, 14 or 15 wherein R⁵ is
15 a 2,6-di(C₁-C₄ alkyl)-4-nitrophenyl group.

18. The compound of Claim 1, wherein R¹ is selected from aryl, substituted aryl, alkyl or cycloalkyl.

20 19. The compound of Claim 16 wherein R⁵ is selected from aryl or substituted aryl.

25 20. The compound of Claim 1, 2, 3, 4, 5, 6, 7, 8,
9, 10 11, 12, 13, 14, 15, 16, 18 or 19 wherein M is
nickel atom or palladium atom.

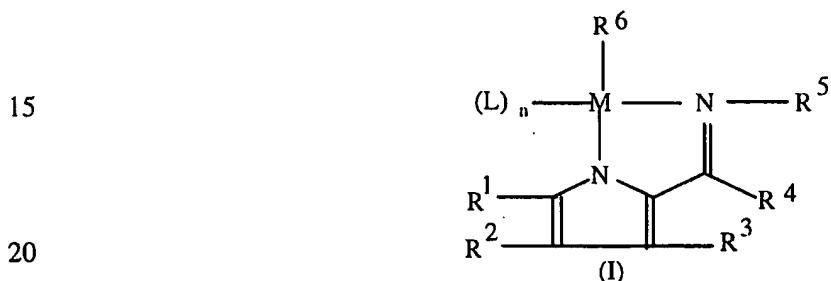
21. The compound of Claim 1 wherein
R¹ is anthracenyl;
R², R³ and R⁴ are each hydrogen;
30 R⁵ is 2,6-di(isopropyl) phenyl;
R⁶ is phenyl;
L is triphenyl phosphine; and
M is selected from nickel or palladium.

22. The compound of Claim 1 wherein
R¹ is phenanthracenyl;
R², R³ and R⁴ are each hydrogen;
R⁵ is 2,6-di(isopropyl) phenyl;
R⁶ is phenyl;
L is triphenyl phosphine; and
M is selected from nickel or palladium.
- 5
23. The compound of Claim 1 wherein
R¹ is phenyl;
R², R³ and R⁴ are each hydrogen;
R⁵ is 2,6-di(isopropyl) phenyl;
R⁶ is phenyl;
L is triphenyl phosphine; and
M is selected from nickel or palladium.
- 10
24. The compound of Claim 1 wherein
R¹ is anthracenyl;
R², R³ and R⁴ are each hydrogen;
R⁵ is 2,6-di(isopropyl)-4-nitrophenyl;
R⁶ is phenyl;
L is triphenyl phosphine; and
M is selected from nickel or palladium.
- 20
25. The compound of Claim 1 wherein
R¹ is nitroanthracenyl;
R², R³ and R⁴ are each hydrogen;
R⁵ is 2,6-di(isopropyl) phenyl;
R⁶ is phenyl;
L is triphenyl phosphine; and
M is selected from nickel or palladium.
- 25
- 30

26. The compound of Claim 1 wherein
R¹ is phenyl;
R², R³ and R⁴ are each hydrogen;
R⁵ is 2,6-di(isopropyl)-4-nitrophenyl;
R⁶ is phenyl;
L is triphenyl phosphine; and
M is selected from nickel or palladium.
- 5
27. The compound of Claim 1 wherein
R¹ is 10-nitroanthracenyl;
R², R³ and R⁴ are each hydrogen;
R⁵ is 2,6-di(isopropyl)-4-nitrophenyl;
R⁶ is phenyl;
L is triphenyl phosphine; and
10 M is selected from nickel or palladium.
- 15
28. The compound of Claim 1 wherein
R¹ is phenanthracenyl;
R², R³ and R⁴ are each hydrogen;
R⁵ is 2,6-di(isopropyl)-4-nitrophenyl;
R⁶ is phenyl;
L is triphenyl phosphine; and
20 M is selected from nickel or palladium.
- 25
29. The compound of Claim 1 wherein
R¹ is terphenyl;
R², R³ and R⁴ are each hydrogen;
R⁵ is 2,6-di(isopropyl) phenyl;
R⁶ is phenyl;
L is triphenyl phosphine; and
30 M is selected from nickel or palladium.

30. The compound of Claim 1 wherein
 R¹ is terphenyl;
 R², R³ and R⁴ are each hydrogen;
 R⁵ is 2,6-di(isopropyl)-4-nitrophenyl;
 5 R⁶ is phenyl;
 L is triphenyl phosphine; and
 M is selected from nickel or palladium.

- 10 31. A process of forming a transition metal
 pyrrolaldimine chelate having the formula:



wherein

- R¹ represents a hydrogen atom; C₁-C₁₁ alkyl; aryl;
 25 substituted aryl wherein the substitution group is selected from C₁-C₄ alkyl, perfluoroalkyl, nitro, sulfonate or halo group; arylalkyl; siloxyl (-OSiA, where A is selected from phenyl or C₁-C₄ alkyl); nitro group; sulfonate group; or halo atom; or a hydrocarbyl
 30 terminated oxyhydrocarbylene group, -(BO)_zR⁷, wherein each B independently is selected from a C₁-C₄ alkylene or an arylene group, O represents oxygen, R⁷ represents a C₁-C₁₁ hydrocarbyl group and z is an integer of 1 to 4;
 R² represents hydrogen atom; aryl; substituted aryl;
 35 C₁-C₁₁ alkyl; halogen atom; or R¹ and R², together, provide a hydrocarbylene or substituted hydrocarbylene which forms an aromatic or non-aromatic carbocyclic ring;
 R³ represents hydrogen;

R⁴ represents hydrogen atom; a C₁-C₁₁ alkyl; an aryl; substituted aryl group; or R³ or R⁴, together, provide a hydrocarbylene or substituted hydrocarbylene forming a non-aromatic carbocyclic ring;

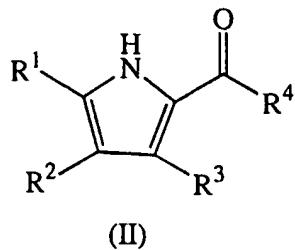
5 R⁵ represents a C₁-C₁₁ alkyl; C₅-C₈ cycloalkyl; aryl group; a substituted aryl having one or both ortho positions of the aromatic group substituted with a C₁-C₄ alkyl, the para position (with respect to the N-R⁵ bond) substituted with a hydrogen, nitro, trifluoromethyl, halogen, methoxy, C₁-C₄ alkyl, sulfonate, or fused or unfused aryl; or a hydrocarbyl terminated oxyhydrocarbylene group -(BO)_nR⁷); or R¹ and R⁵ together form an oxyhydrocarbylene chain, -(BO)_mB-, wherein each B is independently selected from a C₁-C₄ alkylene or an 10 arylene group and m is an integer of 1-4;

15 n represents an integer of 0 or 1;

15 R⁶ represents, when n is 1, an unsubstituted or substituted aromatic group; a C₁-C₁₁ alkyl; a hydrogen atom or halogen atom or when, n is 0, R⁶ represents an allyl 20 group or substituted allyl group;

25 L represents a coordination ligand selected from triphenylphosphine, tri(C₁-C₆ alkyl) phosphine tricycloalkyl phosphine, diphenyl alkyl phosphine, dialkylphenylphosphine, triphenoxyphosphine, trialkylamine, pyridine, C₂-C₅ alkene, substituted C₂-C₄ alkene, diethyl ether, ethyl propyl ether, tetrahydrofuran, or a nitrile; and

30 M represents a Group IV or VIII transition metal selected from Ti, Zr, Hf in the +4 oxidation state or Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt in the +2 oxidation state; comprising reacting an amine of the formula, R⁵NH₂, with an aldehyde of the formula



wherein each R¹, R², R³, R⁴, and R⁵ are as defined above to provide a bidentate ligand;

5 deprotonating said ligand, and contacting the deprotonated product with a transition metal compound having the formula R⁶(L)₂MY wherein each R⁶, L and M are as defined above and Y represents a halogen atom.

10

32. The process of Claim 31 wherein

a) the amine and aldehyde are reacted at a temperature of from 15 to 80°C, for a period of from about 1 to 20 hours in an organic inert solvent;

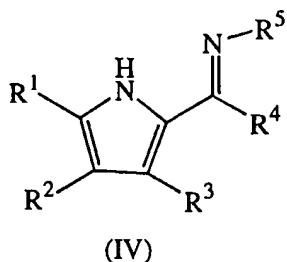
15 b) the ligand is deprotonated by contacting said ligand with an alkyl lithium at a temperature of from about 0°C to about 30°C in an inert solvent; and

c) the transition metal compound and deprotonated product are contacted in an inert solvent at a temperature of from about 10 to 90°C for a period of 1 to 20 hours.

33. The process of Claim 32 wherein step (a) is carried out at 15 to 25°C in a medium selected from C₁-C₅ alkanol, benzene or toluene for a period of 10 to 12 hours; step (b) is carried out at 0 to 10°C with n-butyl lithium in a medium selected from tetrahydrofuran, dialkylether, C₅-C₁₀ hydrocarbon, dioxane, for a period of 5 to 30 minutes; and step (c) is carried out at 10 to 30°C in a medium of tetrahydrofuran, C₅-C₁₀ hydrocarbon, or dialkyl ether, for a period of 10 to 15 hours.

10

34. A compound represented by the formula



15

wherein

R¹ represents a hydrogen atom; C₁-C₁₁ alkyl; aryl; substituted aryl wherein the substitution group is selected from C₁-C₄ alkyl, perfluoroalkyl, nitro, sulfonate or halo group; arylalkyl; or siloxyl (-OSiA, where A is selected from phenyl or C₁-C₄ alkyl); nitro group; sulfonate group; halo atom; or a hydrocarbyl terminated oxyhydrocarbylene group, -(BO)_zR⁷, wherein each B independently is selected from a C₁-C₄ alkylene or an arylene group, O represents oxygen, R⁷ represents a C₁-C₁₁ hydrocarbyl group and z is an integer of 1 to 4;

R² represents hydrogen atom, aryl, substituted aryl, C₁-C₁₁ alkyl, halogen atom or R¹ and R², together, provide a hydrocarbylene or substituted hydrocarbylene which forms an aromatic or non-aromatic carbocyclic ring;

R³ represents hydrogen;

R⁴ represents hydrogen atom, a C₁-C₁₁ alkyl; an aryl; substituted aryl group; or R³ or R⁴, together, provide a hydrocarbylene or substituted hydrocarbylene forming a non-aromatic carbocyclic ring; and

R⁵ represents a C₁-C₁₁ alkyl; cycloalkyl; aryl group; a substituted aryl having one or both ortho positions of the aromatic group substituted with a C₁-C₄ alkyl, the para position (with respect to the N-R⁵ bond) substituted with a hydrogen, nitro, trifluoromethyl, halogen, methoxy or C₁-C₄ alkyl or fused or unfused aryl group; or a hydrocarbyl terminated oxyhydrocarbylene group (-(BO)₂R⁷); or R¹ and R⁵ together form an oxyhydrocarbylene chain (-(BO)_mB-) wherein each B is independently selected from a C₁-C₄ alkylene or an arylene group and m is an integer of 1-4.

35. The compound of Claim 34 wherein R¹ is selected from aryl, substituted aryl or C₁-C₆ alkyl group.

36. The compound of Claim 34 wherein R⁵ is selected from aryl, substituted aryl, C₁-C₁₁ alkyl or C₅-C₈ cycloalkyl.

37. The compound of Claim 35 wherein R⁵ is selected from aryl or substituted aryl.

38. The compound of Claim 35 wherein R⁵ is selected from alkyl or cycloalkyl.

39. The compound of Claim 34 wherein R¹ is selected from t-butyl, anthracenyl, phenanthracenyl, or terphenyl.

40. The compound of Claim 34 wherein R⁵ is 2,6-di(C₁-C₄ alkyl)phenyl group.

41. The compound of Claim 39 wherein R⁵ is 2,6-di(isopropyl)phenyl.

42. The compound of Claim 34 wherein R¹ is selected from a hydrocarbyl terminated oxyhydrocarbylene group represented by the formula -(BO)_zR⁷ wherein each B is independently selected from a C₁-C₄ alkylene or an arylene group, O is oxygen, R⁷ is a C₁-C₁₁ hydrocarbyl and z is 1-4.

43. The compound of Claim 34 wherein R⁵ is selected from an aryl group substituted with a hydrocarbyl terminated oxyhydrocarbylene group represented by the formula -(BO)_zR⁷ wherein each B is independently selected from a C₁-C₄ alkylene or an arylene group, O is oxygen, R⁷ is a C₁-C₁₁ hydrocarbyl and z is 1-4.

44. The compound of Claim 34 wherein R⁵ is selected from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is phenanthracenyl.

45. The compound of Claim 34 wherein R⁵ is selected from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is phenyl.

46. The compound of Claim 43, 44 or 45 wherein R¹ and R⁵ together represent a polyoxyhydrocarbylene group.

47. The compound of Claim 43, 44 or 45 wherein R⁵ is a 2,6-di(C₁-C₄ alkyl)-4-nitrophenyl group.

48. The compound of Claim 34 wherein R¹ and R⁵ together represent a polyoxyhydrocarbylene group.
49. The compound of Claim 34 wherein
5 R¹ is anthracenyl;
R², R³ and R⁴ are each hydrogen; and
R⁵ is 2,6-di(isopropyl) phenyl.
50. The compound of Claim 34 wherein
10 R¹ is phenanthracenyl;
R², R³ and R⁴ are each hydrogen; and
R⁵ is 2,6-di(isopropyl) phenyl.
51. The compound of Claim 34 wherein
15 R¹ is phenyl;
R², R³ and R⁴ are each hydrogen; and
R⁵ is 2,6-di(isopropyl) phenyl.
52. The compound of Claim 34 wherein
20 R¹ is anthracenyl;
R², R³ and R⁴ are each hydrogen; and
R⁵ is 2,6-di(t-butyl) phenyl.
53. The compound of Claim 34 wherein
25 R¹ is 10-nitroanthracenyl;
R², R³ and R⁴ are each hydrogen; and
R⁵ is 2,6-di(isopropyl) phenyl.
54. The compound of Claim 34 wherein
30 R¹ is terphenyl;
R², R³ and R⁴ are each hydrogen; and
R⁵ is 2,6-di(isopropyl) phenyl.

55. The compound of Claim 34 wherein
 R^1 is terphenyl;
 R^2 , R^3 and R^4 are each hydrogen; and
 R^5 is 2,6-di(isopropyl)-4-nitrophenyl.

5

56. The compound of Claim 34 wherein
 R^1 is 10-nitroanthracenyl;
 R^2 , R^3 and R^4 are each hydrogen; and
 R^5 is 2,6-di(isopropyl)-4-nitrophenyl.

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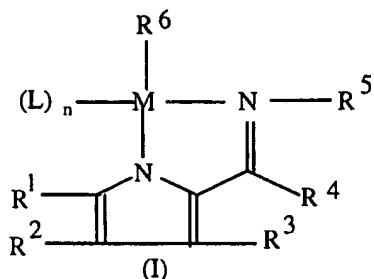
57. The compound of Claim 34, 35, 36, 37, 38, 39,
40, 41, 42, 43, 44 or 45 wherein compound IV is an alkali
metal salt.

15

58. A process for forming a polyolefin comprising
contacting at least one olefinic compound with a catalyst
composition comprising a compound represented by the
general formula:

20

25



wherein

R^1 represents a hydrogen atom; C_1-C_{11} alkyl; aryl;
30 substituted aryl wherein the substitution group is
selected from C_1-C_4 alkyl, perfluoroalkyl, nitro,
sulfonate or halo group; arylalkyl; siloxyl (-OSiA, where
A is selected from phenyl or C_1-C_4 alkyl); nitro group;
sulfonate group; halo atom; or a hydrocarbyl terminated

oxyhydrocarbylene group $-(BO)_zR^7$) wherein each B independently is selected from a C₁-C₄ alkylene or an arylene group, O represents oxygen, R⁷ represents a C₁-C₁₁ hydrocarbyl group and z is an integer of 1 to 4;

5 R² represents hydrogen atom, aryl, substituted aryl, C₁-C₁₁ alkyl, halogen atom or R¹ and R², together, provide a hydrocarbylene or substituted hydrocarbylene which forms an aromatic or non-aromatic carbocyclic ring;

R³ represents hydrogen;

10 R⁴ represents hydrogen atom; a C₁-C₁₁ alkyl; an aryl; substituted aryl group; or R³ or R⁴, together, provide a hydrocarbylene or substituted hydrocarbylene forming a non-aromatic carbocyclic ring;

15 R⁵ represents a C₁-C₁₁ alkyl; C₅-C₈ cycloalkyl; aryl group; a substituted aryl having one or both ortho positions of the aromatic group substituted with a C₁-C₄ alkyl, the para position (with respect to the N-R⁵ bond) substituted with a hydrogen, nitro, trifluoromethyl, halogen, methoxy or C₁-C₄ alkyl, sulfonate or fused or
20 unfused aryl group, or a hydrocarbyl terminated oxyhydrocarbylene group $-(BO)_2R^7$; or R¹ and R⁵ together form an oxyhydrocarbylene chain $-(BO)_mB-$ wherein each B is independently selected from a C₁-C₄ alkylene or an arylene group and m is an integer of 1-4;

25 n represents an integer of 0 or 1;

R⁶ represents, when n is 1, an unsubstituted or substituted aromatic group; a C₁-C₁₁ alkyl; a hydrogen atom or halogen atom or when, n is 0, R⁶ represents an allyl group or substituted allyl group;

L represents a coordination ligand selected from triphenylphosphine, tri(C₁-C₆ alkyl) phosphine, tricycloalkyl phosphine, diphenyl alkyl phosphine, dialkyl phenylphosphine, triphenoxyphosphine, 5 trialkylamine, pyridine, C₂-C₂₀ alkene, substituted C₂-C₆ alkene, C₁-C₁₁ alkoxy, di(C₁-C₆ alkyl) ether, tetrahydrofuran, or a nitrile; and

M represents a Group IV or VIII transition metal selected from Ti, Zr, Hf in the +4 oxidation state or Fe, 10 Co, Ni, Ru, Rh, Pd, Os, Ir, Pt in the +2 oxidation state.

59. The process of Claim 58 wherein the catalyst composition further comprises a phosphine sponge.

15 60. The process of Claim 58 wherein R⁶ represents halogen atom and the composition further comprises a catalyst adjunct selected from a partially hydrolyzed aluminum alkyl compound or an aluminum alkyl or mixture thereof.

20 61. The process of Claim 60 wherein the catalyst adjunct is selected from methyl alumoxane or trialkyl-aluminum or mixture thereof.

25 62. The process of Claim 58 wherein R¹ is selected from aryl group, substituted aryl group or C₁-C₆ alkyl group.

30 63. The process of Claim 59 or 60 wherein R¹ is selected from aryl group, substituted aryl group or C₁-C₆ alkyl group.

64. The process of Claim 62 wherein R⁵ is selected from an aryl group having one or both ortho positions substituted with a C₁-C₄ alkyl group.

5 65. The process of Claim 63 wherein R⁵ is selected from an aryl group having one or both ortho positions substituted with a C₁-C₄ alkyl group.

10 66. The process of Claim 62 wherein R⁵ is selected from alkyl or cycloalkyl.

67. The process of Claim 63 wherein R⁵ is selected from alkyl or cycloalkyl.

15 68. The process of Claim 58, 59, 60, 61 or 62 wherein M is nickel or palladium atom.

69. The process of Claim 68 wherein the olefinic compound is selected from a C₂-C₃ olefinic compound.

20 70. The process of Claim 69 wherein the olefinic compound is ethylene.

25 71. The process of Claim 69 wherein the olefinic compound further comprises at least one functionalized olefin.

72. The process of Claim 71 wherein the functionalized olefin is selected from a carboxylic acid of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{COOH}$, or carboxylic acid ester of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}'$ or $\text{CH}_2=\text{CHOCOR}'$, an alkyl vinyl ether of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{OR}'$, vinyl ketones of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{C(O)R}'$, vinyl alcohol of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{OH}$, vinyl amine of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{NR}^8_2$, wherein m is an integer of 0 to 10 and R' is a $\text{C}_1\text{-C}_{10}$ hydrocarbyl, aryl or substituted aryl group and each R⁸ is independently selected from hydrogen atom or a R' group; a cycloolefin having a functional group selected from an ester, carboxylic acid, halogen atom, or amine group; unsaturated dicarboxylic acid anhydride; carbon monoxide; vinyl halide; or mixtures thereof.

15

73. The process of Claim 58 wherein the catalyst composition further comprises a phosphine sponge or a Lewis base or mixtures thereof.

20

74. The process of Claim 58 wherein the catalyst composition further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates and organonitro compounds and mixtures thereof.

25

75. The process of Claim 58 wherein the catalyst is used in the presence of water and the molar ratio of water to catalyst is from 0 to 10².

30

76. The process of Claim 74 wherein the Lewis base is an ether selected from a di($\text{C}_1\text{-C}_{10}$ alkyl)ether, aryl ethers, aryl alkyl ethers, cyclic ethers, polyethers, or mixtures thereof.

77. The process of Claim 76 wherein the polymerization is carried out in solution and the polymerization solvent comprises an ether or polyether.

5 78. The process of Claim 74 wherein the Lewis base is an organic ester represented by the formula:



wherein each R^9 independently represents a $\text{C}_1\text{-}\text{C}_{11}$ alkyl group.

15 79. The process of Claim 74 wherein the Lewis base is an aldehyde or ketone represented by the formula:



wherein R^{10} represents an unsubstituted or substituted $\text{C}_1\text{-}\text{C}_{12}$ hydrocarbyl group and R^{11} represents a hydrogen atom or an R^{10} group.

25 80. The process of Claim 74 wherein the Lewis base is a monohydric or polyhydric alcohol, said alcohol having hydrocarbyl group composed of a $\text{C}_1\text{-}\text{C}_{12}$ alkyl, aryl, alkaryl or aralkyl group.

30

81. The process of Claim 74 wherein the Lewis base is an amide represented by the formula:



wherein R¹² and R¹³ each independently represents a C₁-C₁₁ hydrocarbyl and R¹⁴ represents hydrogen or a C₁-C₁₁ hydrocarbyl group.

10

82. The process of Claim 74 wherein the Lewis base is an organonitro compound selected from C₁-C₁₁ nitroalkanes, C₁-C₁₁ polynitro alkanes, and mono-nitroaromatics.

15

83. The process of Claim 74, 76, 78, 79, 80, 81 or 82 wherein the Lewis base is present in a molar ratio of Lewis base to catalyst compound I of from about 10° to about 10⁴.

20

84. The process of Claim 58 wherein R¹ is selected from a hydrocarbyl terminated oxyhydrocarbylene group represented by the formula -(BO)_zR⁷ wherein each B is independently selected from a C₁-C₄ alkylene or an arylene group, O is oxygen, R⁷ is a C₁-C₁₁ hydrocarbyl and z is 1-4.

25

85. The process of Claim 58 wherein R⁵ is selected from an aryl group substituted with a hydrocarbyl terminated oxyalkylene group represented by the formula -(BO)_zR⁷ wherein B is a C₁-C₄ alkylene, O is oxygen, R⁷ is a C₁-C₁₁ hydrocarbyl and z is 1-4.

86. The process of Claim 58 wherein R⁵ is selected from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is anthracenyl.

5 87. The process of Claim 58 wherein R⁵ is selected from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is phenanthracenyl.

88. The process of Claim 58 wherein R⁵ is selected from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is phenyl.

10

89. The process of Claim 58 wherein R¹ and R⁵ together represent a polyoxyhydrocarbylene group.

15

90. The process of Claim 59, 60, 61, 62, 64, 65, 66, 67 or 68 wherein the catalyst composition further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates, organonitro compounds and mixtures thereof.

20

91. The process of Claim 63 wherein the catalyst composition further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates, organonitro compounds and mixtures thereof.

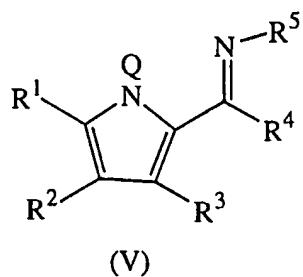
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92. The process of Claim 84 or 85 wherein the catalyst composition further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates, organonitro compounds and mixtures thereof.

30

93. A process for forming a polyolefin comprising contacting at least one olefinic compound with a catalyst composition comprising:

(A) a compound represented by the formula:



5 wherein

R¹ represents a hydrogen atom; C₁-C₁₁ alkyl; aryl; substituted aryl wherein the substitution group is selected from C₁-C₄ alkyl, perfluoroalkyl, nitro, sulfonate or halo group; arylalkyl; or siloxyl (-OSiA, where A is selected from phenyl or C₁-C₄ alkyl); nitro group; sulfonate group; halo atom; or or a hydrocarbyl terminated oxyhydrocarbylene group $-(BO_zR^7)$, wherein each B independently is selected from a C₁-C₄ alkylene or an arylene group, O represents oxygen, R' represents a C₁-C₁₁ hydrocarbyl group and z is an integer of 1 to 4;

R² represents hydrogen atom, aryl, substituted aryl, C₁-C₁₁ alkyl, halogen atom or R¹ and R², together, provide a hydrocarbylene or substituted hydrocarbylene which forms an aromatic or non-aromatic carbocyclic ring;

20 R³ represents hydrogen;

R⁴ represents hydrogen atom, a C₁-C₁₁ alkyl; an aryl; substituted aryl group; or R³ or R⁴, together, provide a hydrocarbylene or substituted hydrocarbylene forming a non-aromatic carbocyclic ring;

R⁵ represents a C₁-C₁₁ alkyl; cycloalkyl; aryl group; a substituted aryl having one or both ortho positions of the aromatic group substituted with a C₁-C₄ alkyl, the para position (with respect to the N-R⁵ bond) substituted
5 with a hydrogen, nitro, trifluoromethyl, halogen, methoxy or C₁-C₄ alkyl or fused or unfused aryl; or a hydrocarbyl terminated oxyhydrocarbylene group (-(BO)₂R⁷); or R¹ and R⁵ together form an oxyhydrocarbylene chain (-(BO)_mB-) wherein each B is independently selected from a C₁-C₄
10 alkylene or an arylene group and m is an integer of 1-4); and

Q is an alkali metal cation or hydrogen; and

(B) a transition metal organic complex, wherein said transition metal has a valence state of + 2 or +4
15 and is selected from a Group IV or VIII transition metal of Ti, Zr, Hf, Co, Ni, Ru, Rh, Pd, Os, Ir or Pt.

94. The process of Claim 93 wherein the transition metal organic complex is a complex represented by a
20 formula R⁶(L)₂MY wherein

R⁶ represents an unsubstituted or substituted aromatic group; a C₁-C₁₁ alkyl; an allyl or substituted allyl group;

L represents a coordination ligand selected from triphenylphosphine, tri (C₁-C₆ alkyl) phosphine, tricycloalkyl phosphine, diphenyl alkyl phosphine, dialkyl phenylphosphine, triphenoxyphosphine, trialkylamine, pyridine, C₂-C₂₀ alkene, substituted C₂-C₄ alkene, C₁-C₄ alkoxy, di-(C₁-C₃ alkyl) ether,
30 tetrahydrofuran, or a nitrile;

Y represents a halogen atom selected from chloro, bromo or fluoro; and

M represents a transition metal selected from a Group IV or Group VIII metal of Ti, Zr, Hf, Co, Ni, Ru, Rh, Pd, Os, Ir or Pt.

5 95. The process of Claim 93 or 94 wherein the catalyst composition further comprises a phosphine sponge.

10 96. The process of Claim 94 wherein the complex is bis-triphenylphosphine nickel (phenyl) chloride.

15 97. The process of Claim 94 wherein the composition further comprises a catalyst adjunct selected from a partially hydrolyzed aluminum alkyl compound or an aluminum alkyl or mixture thereof.

20 98. The process of Claim 97 wherein the catalyst composition further comprises an adjunct selected from methyl alumoxane or trialkylaluminum or mixture thereof.

99. The process of Claim 93 wherein R¹ is selected from aryl group, substituted aryl group or C₁-C₆ alkyl group.

25 100. The process of Claim 94 or 98 wherein R¹ is selected from aryl group, substituted aryl group or C₁-C₆ alkyl group.

30 101. The process of Claim 99 wherein R⁵ is selected from an aryl group having one or both ortho positions substituted with a C₁-C₄ alkyl group.

102. The process of Claim 100 wherein R⁵ is selected from an aryl group having one or both ortho positions substituted with a C₁-C₄ alkyl group.

5 103. The process of Claim 99 wherein R⁵ is selected from alkyl or cycloalkyl.

104. The process of Claim 100 wherein R⁵ is selected from alkyl or cycloalkyl.

10 105. The process of Claim 93, 94, 96, 97 or 98 wherein the transition metal of said complex is selected from nickel or palladium atom.

15 106. The process of Claim 105 wherein the olefinic compound is a C₂-C₆ olefinic compound.

107. The process of Claim 106 wherein the olefinic compound is ethylene.

20 108. The process of Claim 106 wherein the olefinic compound further comprises at least one functionalized olefin.

109. The process of Claim 108 wherein the functionalized olefin is selected from a carboxylic acid of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{COOH}$, or carboxylic acid ester of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}'$ or $\text{CH}_2=\text{CHOCOR}'$, an alkyl vinyl ether of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{OR}'$, vinyl ketones of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{C(O)R}'$, vinyl alcohol of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{OH}$, vinyl amine of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{NR}^b_2$, wherein m is an integer of 0 to 10 and R' is a $\text{C}_1\text{-}\text{C}_{10}$ hydrocarbyl, aryl or substituted aryl group and each R^b is independently selected from hydrogen atom or a R' group; a cycloolefin having a functional group selected from an ester, carboxylic acid, halogen atom, hydroxyl group, or amine group; unsaturated dicarboxylic acid anhydride; carbon monoxide; vinyl halide; or mixtures thereof.

110. The process of Claim 108 wherein the functionalized olefin is a hydroxyl substituted or ester substituted norbornene.

111. The process of Claim 93 wherein the transition metal organic complex is a complex of a $\text{C}_5\text{-}\text{C}_{10}$ cycloalkyldiene, or a trihydrocarbyl phosphine wherein each hydrocarbyl group is independently selected from $\text{C}_1\text{-}\text{C}_{10}$ alkyl, cycloalkyl or phenyl group.

112. The process of Claim 93 wherein the catalyst composition further comprises a phosphine sponge or a Lewis base or mixtures thereof.

113. The process of Claim 93 wherein the catalyst composition further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates and organonitro compounds and mixtures thereof.

5

114. The process of Claim 93 wherein the catalyst is used in the presence of water and the molar ratio of water to catalyst is from 0 to about 10³.

10

115. The process of Claim 113 wherein the Lewis base is an ether selected from di(C₁-C₁₈ alkyl) ethers, aryl ethers, aryl alkyl ethers, cyclic ethers, polyethers, or mixtures thereof.

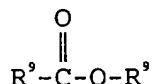
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116. The process of Claim 115 wherein the polymerization is carried out in solution and the polymerization solvent comprises an ether or polyether.

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117. The process of Claim 113 wherein the Lewis base is an organic ester represented by the formula:

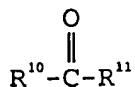
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wherein each R' independently represents a C₁-C₁₈ alkyl group.

118. The process of Claim 113 wherein the Lewis base is an aldehyde or ketone represented by the formula:

5



wherein R¹⁰ represents an unsubstituted or substituted C₁-C₁₂ hydrocarbyl group and R¹¹ represents a hydrogen atom or 10 an R¹⁰ group.

15

119. The process of Claim 113 wherein the Lewis base is a monohydric or polyhydric alcohol, said alcohol having a hydrocarbyl group composed of a C₁-C₁₂ alkyl, aryl, alkaryl or aralkyl group.

20



25

wherein R¹² and R¹³ each independently represents a C₁-C₁₁ hydrocarbyl and R¹⁴ represents hydrogen or a C₁-C₁₁ hydrocarbyl group.

30

121. The process of Claim 113 wherein the Lewis base is an organonitro compound selected from C₁-C₁₁ nitroalkanes, C₁-C₁₁ polynitro alkanes, and mono-nitroaromatics.

35

122. The process of Claim 113, 115, 117, 118, 119, 120 or 121 wherein the Lewis base is present in a molar ratio of Lewis base to compound V from about 10⁰ to about 10⁴.

123. The process of Claim 93 wherein R¹ is selected from a hydrocarbyl terminated oxyhydrocarbylene group represented by the formula -(BO)_zR⁷ wherein each B is independently selected from a C₁-C₄ alkylene or an arylene, O is oxygen, R⁷ is a C₁-C₁₁ hydrocarbyl and z is 1-4.

10 124. The process of Claim 93 wherein R⁵ is selected from an aryl group substituted with a hydrocarbyl terminated oxyalkylene group represented by the formula -(BO)_zR⁷ wherein B is a C₁-C₄ alkylene, O is oxygen, R⁷ is a C₁-C₁₁ hydrocarbyl and z is 1-4.

15 125. The process of Claim 93 wherein R⁵ is selected from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is anthracenyl.

20 126. The process of Claim 93 wherein R⁵ is selected from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is phenanthracenyl.

127. The process of Claim 93 wherein R⁵ is selected from a 2,6-di(C₁-C₄ alkyl) phenyl and R¹ is phenyl.

25 128. The process of Claim 93 wherein R¹ and R⁵ together represent a polyoxyhydrocarbylene group.

101, 102, 103 or 104 wherein the catalyst composition
30 further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates, organonitro compounds and mixtures thereof.

130. The process of Claim 95 wherein the catalyst composition further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates, organonitro compounds and mixtures thereof.

131. The process of Claim 112, 123 or 124 wherein the catalyst composition further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates, organonitro compounds and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03175

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.

US CL :502/155, 167; 525/245, 248; 526/170, 171; 548/402, 453

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/155, 167; 525/245, 248; 526/170, 171; 548/402, 453

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,557,023 A (SOMOGYVARI et al) 17 September 1996.	1-131
A	US 4,537,982 A (STARZEWSKI et al) 27 August 1985.	1-131
A	US 4,382,153 A (BEACH et al) 03 May 1983.	1-131
A	US 3,686,159 A (BAUER et al) 22 August 1972.	1-131

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

04 JUNE 1998

Date of mailing of the international search report

22 JUN 1998

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/03175

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

C07D 207/00, 209/00, 487/02, 491/02, 495/02, 497/02; B01J 31/00; C08F 4/00